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ANHYDROUS CALCIUM DIOXIDE AND THE CONSTITUTION OF ITS HYDRATES

de Forcrand

Translation of "Sur le Bioxyde de Calcium Anhydre
et la Constitution de ses Hydrates"
Comptes Rendus, Vol. 130, pp. 1388-1391, 1900.

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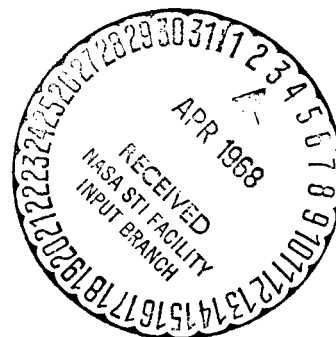
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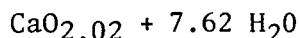
de Forcrand

ABSTRACT: Anhydrous CaO_2 is dissolved in HCl to determine the heat of solution. The stability and heat of formation of CaO_2 and its hydrates are determined, and compared to analogous compounds of strontium and barium.

I. The hydrated precipitate of calcium dioxide $\text{CaO}_2 + 8\text{H}_2\text{O}$, which I investigated earlier, is capable of losing its crystallization water and of yielding anhydrous calcium dioxide. /1388*

To prevent it from giving up oxygen as a result of the heating effect, I had to desiccate it under a vacuum desiccator in the presence of phosphoric anhydride.

The hydrate used consisted of



which came in pearl-shaped flakes. I prepared it by using 4 H_2O_2 in solution over CaO .

At the end of six days the dioxide formed an amorphous dry powder which upon analysis yielded the following:

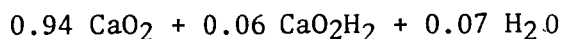
Ca	54.45%
O as it pertains to CaO	21.78%
O in the dioxide state	20.45%
H_2O (balance)	3.32%

which yields the formula

/1389



or



i.e. essentially anhydrous CaO_2 .

*Numbers in the margin indicate pagination in the foreign text.

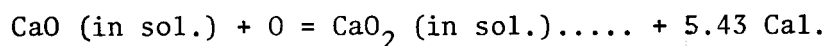
I did not push the dehydration any further since the dioxide had already lost its oxygen traces under cooling.

I dissolved this compound in a calculated amount of hydrochloric acid diluted for exact neutralization.

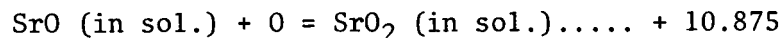
Taking into account the small amount of protoxide hydrate contained in it, I found

$$18.930 \text{ Cal for } \text{CaO}_2$$

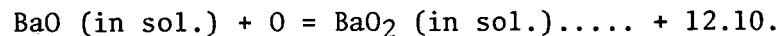
Knowing the heat of solution of CaO in acid and the heat of formation of hydrogen peroxide, the following reaction can be calculated:



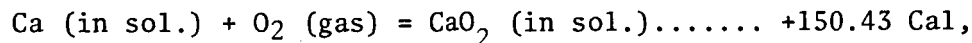
Earlier I had found



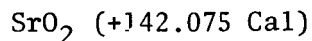
and Berthelot reported



Thus, starting with anhydrous protoxide, the stability of the anhydrous dioxide increases as the atomic weight rises from calcium to barium. It is further known that barium dioxide alone can be obtained directly by passing free oxygen over BaO and furthermore under certain temperature limitations. Lime and strontium oxide cannot be dioxidized directly. This also explains why, particularly with calcium dioxide hydrates, one cannot obtain absolutely anhydrous dioxide, since during the last phase of the vacuum desiccation the hydrate loses some oxygen and the stability of the dioxide becomes comparable to that of hydrate. Moissan provided the value of the heat of formation of anhydrous lime ($\text{Ca} + \text{O} = 145 \text{ Cal}$). Starting with the elements, we can make the following calculation:



a number which is slightly higher than that resulting from



if the Thomsen data were to be observed: $\text{Sr} + \text{O} = +131.2 \text{ Cal}$, which, however, /1390 is probably very close.

II. Let us now examine the two successive hydration states: CaO_2 , $2\text{H}_2\text{O}$ and CaO_2 , 8 or 9 H_2O , already described by Thenard and by Schoene. For the most hydrated compound we obtain the following:

$\text{CaO}_2 \text{ (in sol.)} + 8 \text{ H}_2\text{O (liq.)}^1 = \text{CaO}_2, 8 \text{ H}_2\text{O (in sol.)} \dots +15.636 \text{ Cal}$

$\text{CaO}_2 \text{ (in sol.)} + 8 \text{ H}_2\text{O (in sol.)} = \text{CaO}_2, 8 \text{ H}_2\text{O (in sol.)} \dots +4.196 \text{ Cal}$

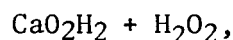
i.e. for 1 $\text{H}_2\text{O (liq.)} + 1.954 \text{ Cal}$ and for 1 $\text{H}_2\text{O (in sol.)} \dots +0.524 \text{ Cal}$

These numbers are very close to those which yield the two other dioxides ².

However, if we calculate the transition from the first state to the second (2 H_2O to 8 H_2O), we find 6 $\text{H}_2\text{O (liq. fixed)} + 17.851 \text{ Cal}$, i.e. +2.975 Cal for each molecule of water.

This number is higher than 1.954 Cal which is not tolerable. Consequently the fixation of the first two molecules of water on $\text{CaO}_2 \text{ (in sol.)}$ would absorb -2.215 Cal while the six latter molecules would release +15.636 Cal.

This conclusion must be discarded and the conclusion should be drawn that the first compound $\text{CaO}_2, 2 \text{ H}_2\text{O}$ is not a real dioxide hydrate, but a combination of hydrogen peroxide and lime hydrate



which explains its varying properties.

The heat of formation of this compound can even be calculated with the data which I published

$\text{CaO}_2\text{H}_2 \text{ (in sol.)} + \text{H}_2\text{O}_2 \text{ (diss.)} = \text{CaO}_2\text{H}_2, \text{H}_2\text{O}_2 \text{ (in sol.)} \dots +9.815 \text{ Cal.}$

I have explained earlier that this particular compound is produced between +10° and +16° if hydrogen peroxide is added to lime in solution without exceeding the 2 H_2O_2 amount, or by exceeding it while increasing the temperature to 20° so that the only true hydrate with 8 H_2O is formed only with 3 or 4 molecules of hydrogen peroxide and at low temperature.

This leads to a supplementary release of heat of +17.851 Cal, but this does not correspond to a simple addition of 6 molecules of water; actually, the work produced now is the following:

/1391

Absorption	
	Cal
Destruction of the compound $\text{CaO}_2\text{H}_2, \text{H}_2\text{O}_2$	- 9.815
Dehydration of CaO_2H_2	- 15.100
Total	- 24.915

¹I am assuming here preferably 8 H_2O since analyses sometimes gave me more sometimes less than 8 H_2O .

²SrO yielded +2.275 Cal for 1 $\text{H}_2\text{O (liq.)}$ and BaO + 1.82 Cal (Comptes rendus, Vol. 130, p. 1,019).

Realease	
	Cal
Destruction of H_2O_2 (diss.)	+ 21.7
Combination of oxygen with CaO (in sol.)	+ 5.43
Hydration of CaO_2 (in sol.)	+ <u>15.636</u>
Total	+ 42.766

Finally, this means $+42.766 \text{ Cal} - 24.915 \text{ Cal} = +17.851 \text{ Cal}$ of which only $+15.636 \text{ Cal}$ represents the amount of heat released for the hydration per 8 molecules of water, corresponding to a rather unstable hydrate.

The strontium and barium dioxides do not exhibit any complexity of this type.

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